GROUP 17

Physical properties of the Group 17 elements

The Group 17 elements are also known as the halogens.

Colours and trends in volatility

At room temperature, the colours of the halogens get darker down the group. The boiling points also increase due to the increasing strength of the **intermolecular forces.**

- **Fluorine** - pale yellow gas
- **Chlorine** - green gas
- **Bromine** - red-brown liquid
- **Iodine** - grey solid

Volatility and van der Waals

Fluorine has the lowest melting and boiling points in group 7 and is therefore the **most volatile**. This is because it has the **weakest van der Waals** (intermolecular) forces.
The number of electrons in each molecule and the size of the molecules increases down group 7. This means that the **temporary dipoles** get stronger so there are more **van der Waals forces** between molecules. More energy is needed to overcome these forces so **volatility decreases** down Group 17.

Chemical properties of the elements and their hydrides

Reactivity of the elements as oxidising agents

When the halogens react, they **gain an electron** to form negative ions. **Reactivity** of the halogen **decreases** down the group. This is because it becomes harder to gain an electron as **electron shielding** and **atomic radius** increase down the group so there is weaker attraction between the incoming electron and the protons in the nucleus.

Oxidising agents are elements/ compounds that gain electrons to oxidise another element/ compound. Halogens act as oxidising agents and they become **less oxidising down the group** due to the decreasing reactivity. The relative oxidising strengths of the halogens can be seen by their **displacement** reactions with other halide ions.

The table below shows that out of chlorine, bromine and iodine, **chlorine** is the **strongest oxidising agent** and iodine is the weakest:

Halogen	Displacement	Ionic equation
Cl	Chlorine (Cl_2) will displace bromide and iodide ions.	$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$ $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$
Br	Bromine (Br_2) will displace iodide ions.	$Br_2 + 2I^- \rightarrow 2Br^- + I_2$
I	Iodine (I_2) will not react with chloride or bromide ions	No reactions take place

From this table, you can observe the **basic trend**:
'A halogen will displace a halide from a solution if the halide ion is below it in the periodic table.'
Displacement reactions can be identified by a **change in the colour** of the solution.

Chlorine solution - **colourless**
Bromine solution - orange
Iodine solution - **brown**

For example, if chlorine is added to a solution of potassium bromide, the solution will change from colourless to orange due to the formation of bromine:
$Cl_2 + 2KBr \rightarrow Br_2 + 2KCl$

Reaction with hydrogen

The halogens react with hydrogen to form **hydrogen halides**. These reactions show that **reactivity decreases** down Group 17.
The standard reaction equation for the reaction with hydrogen (where X is the halogen) is:

$$X_2 + H_2 \rightarrow 2HX$$

- **Fluorine** reacts **explosively** with hydrogen to form hydrogen fluoride gas. This reaction occurs even in a **cold** atmosphere.
- **Chlorine** reacts with hydrogen if **lightly heated** or exposed to **sunlight**.
- **Bromine** reacts with hydrogen if **heated** with a flame.
- **Iodine** only partially reacts with hydrogen when **constantly heated**. There is a **partial reaction** because an **equilibrium** is set up:
  $I_2 + H_2 \rightleftharpoons 2HI$

Thermal stability of the hydrides

The **thermal stability** of a hydride is how easy a hydrogen halide is broken up into its constituent elements when heated.

- **Hydrogen fluoride** and **hydrogen chloride** are **very thermally stable**. They will not split into hydrogen and the halogen if heated under laboratory conditions.
- **Hydrogen bromide** will **split** into hydrogen and bromine when **heated**.
- **Hydrogen iodide** will split into hydrogen and iodine **more easily than hydrogen bromide**.

These reactions show that **thermal stability of the hydrides decreases down Group 17**. This is because further down the group, the **covalent bonds are weaker** so they can be broken more easily upon heating. The bonds are weaker further down the group because the halogen atoms get larger. This means that the **bonding pair gets further away from the nucleus** so the attraction gets **weaker** and the bond is easier to break.

Bond energies

Bond enthalpies of the hydrides

The thermal stability of the halogens decreases down the group. This can be explained in terms of bond energies (also known as bond enthalpies). Bond enthalpies of the hydrogen halides **decrease** down Group 17 because the size of the halogen **increases**. This means less energy is required to break the covalent bond between hydrogen and halogen.

Bond enthalpies of the halogens

The **bond enthalpies** of the halogen molecules **decrease** from Cl_2 to I_2. This is because the size of the molecules **increases** so the bonding pair is further from the nucleus. In the same way as the hydrogen halides, the **bonding pair is less attracted** to the nucleus in larger molecules so the covalent bond is more easily broken.

Reactions of the halide ions

Reactions with silver nitrate followed by aqueous ammonia

Silver nitrate solution can be used to **test for halide ions** in a solution:

1. Add **nitric acid** to the halide ion solution to remove any ions which may produce a false positive for the test (e.g. carbonate ions).
2. Add a few drops of **silver nitrate** solution ($AgNO_3$).
3. Observe the **precipitate** formed.

The standard equation for this reaction (where X is the halide ion) is:

$$Ag^+_{(aq)} + X^-_{(aq)} \rightarrow AgX_{(s)}$$

Observations:

- **Fluoride** ions - no precipitate.
- **Chloride** ions - white precipitate.
- **Bromide** ions - cream precipitate.
- **Iodide** ions - yellow precipitate.

To ensure the precipitates have been correctly identified, **aqueous ammonia** can be added:

- **Chloride precipitate** - dissolves in dilute NH_3.
- **Bromide precipitate** - dissolves in concentrated NH_3.
- **Iodide precipitate** - insoluble in dilute and concentrated NH_3.

Reactions with concentrated sulfuric acid

All halide ions react with **concentrated sulfuric acid** to produce a **hydrogen halide**. A secondary reaction then takes place, which differs depending on which halide.

Reaction of **NaCl** and **NaF** with H_2SO_4

$NaF + H_2SO_4 \rightarrow NaHSO_4 + HF$

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

For both of these reactions, HF and HCl can be identified as **misty fumes**.
HF and HCl are **not strong enough reducing agents** so no further reactions occur.

Reaction of **NaBr** with H_2SO_4

$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$

Misty fumes of HBr are produced. HBr is a strong enough **reducing agent** to react with H_2SO_4. This second reaction produced the **choking gas SO_2** and **brown fumes of Br_2** in a **redox reaction**:

$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

Reaction of **NaI** with H_2SO_4

$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$

Misty fumes of HI are produced. HI is a strong enough **reducing agent** to react with the H_2SO_4. Similarly to the reaction above, **SO_2** is produced. Since HI is a **very strong reducing agent,** the SO_2 is further reduced to **H_2S** - which smells of **rotten eggs**.

$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

$6HI + SO_2 \rightarrow H_2S + 3I_2 + 2H_2O$

Reactions of chlorine with aqueous sodium hydroxide

A **disproportionation** reaction is a reaction in which an element is both **oxidised** and **reduced**.

Chlorine reacts with cold dilute sodium hydroxide:

$$2NaOH_{(aq)} + Cl_{2\,(g)} \rightarrow NaClO_{(aq)} + NaCl_{(aq)} + H_2O_{(l)}$$

This is a **disproportionation** reaction because chlorine has been **reduced** from 0 in Cl_2 to -1 in NaCl and **oxidised** from 0 in Cl_2 to +1 in NaClO. NaClO (also known as **sodium chlorate(I)** solution) is **bleach**. It is used in water treatment, to bleach textiles and paper, and for cleaning because it **kills bacteria.**

Chlorine also reacts with hot concentrated sodium hydroxide:

$$6NaOH(aq) + 3Cl_{2(g)} \rightarrow 5NaCl(aq) + NaClO_{3(aq)} + 3H_2O(l)$$

This is a **disproportionation** reaction because chlorine has been **reduced** from 0 in Cl_2 to -1 in NaCl and **oxidised** from 0 in Cl_2 to +5 in $NaClO_3$.

Chlorine in water purification

Chlorine is used in water purification because it **kills bacteria.**
Chlorine reacts with water in a **disproportionation** reaction, producing chloride and chlorate ions. The reaction produces HCl so an **alkali** is usually added to the water to **reduce the acidity**.

$$Cl_2 + H_2O \rightleftharpoons 2H^+ + Cl^- + ClO^-$$

Chlorate ions kill bacteria so treating water with chlorine or chlorate ions makes it safe to drink or swim in.

Chlorine treats water in different ways:

- **Kills dangerous microorganisms** which could cause diseases.
- Some chlorine persists in the water which **prevents reinfection** in the long term.
- Prevents the growth of **algae.**
- **Removes bad tastes** and smells.
- Removes **discolouration**.

Chlorine is toxic so there are discussions about whether chlorine should be added to water. In addition to this, chlorine can react with organic matter in the water forming potentially cancer causing compounds. On balance, since only a small amount of chlorine is added, it is agreed that the benefits outweigh the risks.

Industrial importance and environmental significance of the halogens and their compounds

Killing bacteria

Chlorine and chlorate ions are industrially important as they are used to kill bacteria, **preventing disease and infection**.

PVC

Organic compounds containing chlorine are very important. The polymer poly(chloroethene), PVC, contains **one chlorine atom** in each polymer unit and is relied upon for many uses. It is very **hard** so can be used for **windows** and **drain pipes.**
Plasticiser can be added to PVC to make it more **flexible** which extends its uses to other things like **electrical cable insulation** and **clothing**.

Halogenated hydrocarbons

Halogens react with alkanes to form **halogenoalkanes**.
Chlorofluorocarbons (CFCs) are halogenoalkane molecules in which all hydrogen atoms have been replaced by chlorine and fluorine. CFCs were used as **coolants in fridges** and as **solvents** and propellants in **aerosols**. However, CFCs cause **damage to the ozone layer** so they have been banned and replaced with HFCs (**hydrofluorocarbons**) which don't contain chlorine.

Damage to the ozone layer:

Ozone (O_3) is the layer in the upper atmosphere which **absorbs a lot of UV radiation** from the sun, preventing it from reaching us. This is a crucial part of the atmosphere which prevent people getting too much **sun damage.**

Ozone is formed when an **oxygen molecule reacts with an oxygen free radical** (which is produced from an oxygen molecule in the presence of UV light):

$$O_2 \rightarrow O^{\cdot} + O^{\cdot}$$

$$O_2 + O^{\cdot} \rightarrow O_3$$

Chlorine free radicals are formed in the upper atmosphere when CFCs are broken down by UV radiation:

$$CCl_3F \rightarrow Cl^{\cdot} + CCl_2F^{\cdot}$$

The chlorine free radicals react with ozone, **breaking it down into oxygen**. This creates holes in the protective ozone layer.

$$Cl^{\cdot} + O_3 \rightarrow O_2 + ClO^{\cdot}$$

$$ClO^{\cdot} + O_3 \rightarrow 2O_2 + Cl^{\cdot}$$

Overall: $2O_3 \rightarrow 3O_2$